

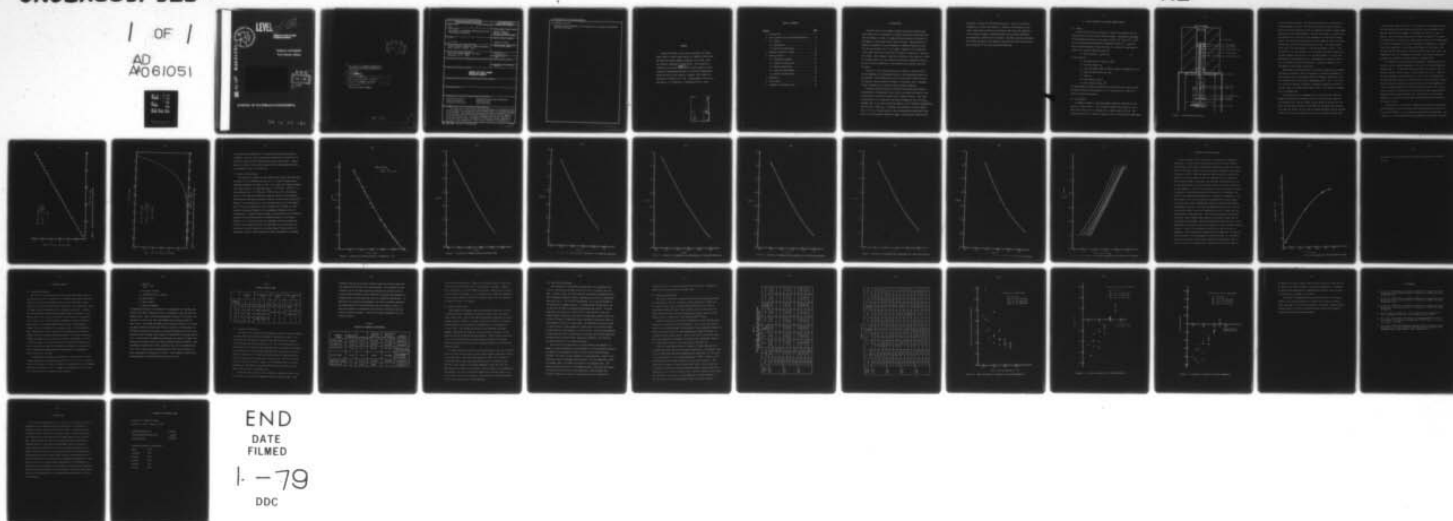
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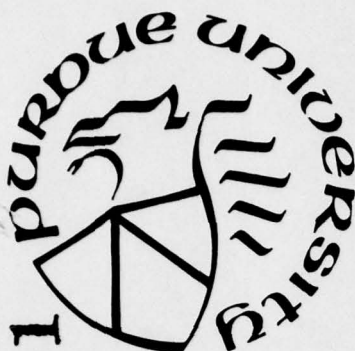
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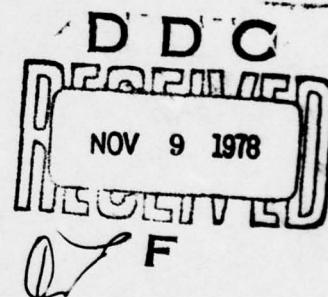
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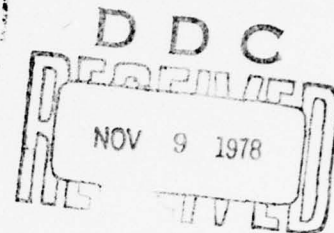
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West Lafayette, Indiana



**SCHOOL OF MATERIALS ENGINEERING**

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6 THE EFFECTS OF SUBSTRATE COMPOSITION  
ON THICK FILM CIRCUIT RELIABILITY

10 R. W. Vest

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)  The viscosity of the resistor glass was measured as a function of dissolved AlSiMag 614 substrate from the softening point to the annealing point of the glasses. The isothermal viscosity was found to increase by a factor of 20 for glass with 10w/o dissolved substrate relative to the standard lead borosilicate glass. The sheet resistances and hot and cold TCRs of thick film resistors were determined as a function of glass composition at seven firing temperatures. These results indicate a retardation of		



20 Abstract (cont'd)

microstructure development in the resistors as the amount of dissolved substrate increases.

# FORWARD

Research described in this report consitutes the second three months of effort under Contract No. N00019-78-C-0236 with the Naval Air Systems Command, Department of the Navy, under the technical cognizance of James Willis. The research was conducted in the Turner Laboratory for Electroceramics, School of Materials Engineering and School of Electrical Engineering, Purdue University, West Lafayette, Indiana 47907, under the direction of Professor R. W. Vest. Contributing to the project were Messrs. J. M. Himelick, P. Palanisamy and R. L. Reed.

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## TABLE OF CONTENTS

<u>Section</u>	<u>Page</u>
1. Introduction . . . . .	1
2. Glass Viscosity by the Beam Bending Method . . .	3
2.1 General . . . . .	3
2.2 Experimental . . . . .	3
2.3 Results and Discussion . . . . .	9
3. Substrate Solubility Studies . . . . .	18
4. Resistor Studies . . . . .	21
4.1 Formulation Blending . . . . .	21
4.2 Conductive Terminations . . . . .	23
4.3 Resistor Fabrication . . . . .	25
4.4 Electrical Measurements . . . . .	26
4.5 Results and Discussion . . . . .	27
5. References . . . . .	34
6. Future Plans . . . . .	35
7. Statement of Estimated Costs . . . . .	36

## 1. INTRODUCTION

The print and fire processing of thick film circuits ensures that there always will be some degree of chemical interaction between the film and the substrate, because all common substrate materials are soluble to some degree in the glasses used in thick film inks. This interaction is primarily responsible for the development of adhesion between the thick film and the substrate, but it also leads to changes in the composition of the glass with the net result that the physical properties of the glass will change. These changes in physical properties of the glass will result in modified kinetics for the various microstructure development processes and all electrical properties of the resistors are related to the microstructure.

The goal of this research program is to develop a sufficient level of understanding of the phenomena involved so that appropriate models can be developed. These models should lead to the writing of specifications for impurity limits and additive ranges for substrates, and to recommendations concerning glass composition and processing conditions.

Previously reported studies [1-3] under this program have primarily concentrated on the magnitude of the effects resulting from chemical interaction between a thick film resistor and a ceramic substrate. The rates of dissolution of two substrates, 96%  $\text{Al}_2\text{O}_3$  (AlSiMag 614) and 99.5%  $\text{Al}_2\text{O}_3$  (AlSiMag 772), in two lead borosilicate glasses (63 w/o  $\text{PbO}$ -25w/o  $\text{B}_2\text{O}_3$ -12w/o  $\text{SiO}_2$  and 70w/o  $\text{PbO}$  - 20w/o  $\text{B}_2\text{O}_3$  - 10w/o  $\text{SiO}_2$ ) were measured at various temperatures. The rate limiting steps for each substrate-glass system were determined in all appropriate temperature ranges, and analytical equations were

developed to predict the substrate recession as a function of time and temperature for thick film resistors. Studies of the influence of substrate constituents dissolved in the glass on the electrical properties of the resistors showed a significant effect on both sheet resistance and temperature coefficient of resistance. The sheet resistance increased and the TCR decreased as the amount of substrate dissolved in the resistor glass increased for the same processing conditions.



## 2. GLASS VISCOSITY BY THE BEAM BENDING METHOD

### 2.1 General

Trouton [4] was the first researcher to derive an expression for the viscous traction of horizontally supported beams. Experimental techniques for determining viscosities in the range of  $10^8$  to  $10^{15}$  poise ( $10^7$  to  $10^{14}$  Pa·s) by measuring beam bending were described by Hagy [5]. A modified form of Hagy's expression for the viscosity of a centrally loaded beam in terms of its mid-point deflection rate is:

$$\eta = (g\ell^3/144I_c v)[L + (\rho_g A\ell/1.6)] \quad (1)$$

In this equation:

$g$  = acceleration due to gravity,  $\text{cm/s}^2$

$\ell$  = free span length, cm

$I_c$  = cross sectional moment of inertia (width x thickness<sup>3</sup>/12),  $\text{cm}^4$

$v$  = mid-point deflection rate,  $\text{cm/s}$

$L$  = load, gm

$\rho_g$  = glass density,  $\text{gm/cm}^3$

$A$  = cross sectional area,  $\text{cm}^2$

The beam bending viscometer described in the following section was designed to measure the mid-point deflection,  $v$ , of a glass beam as a function of time at elevated temperatures.

### 2.2 Experimental

A schematic diagram of the beam bending viscometer developed for this project is shown in Fig. 1. The viscometer assembly was housed in a clam shell tube furnace 10 cm in diameter with a heated length of 60 cm. The furnace was mounted on a wheeled support so that it could be moved independent

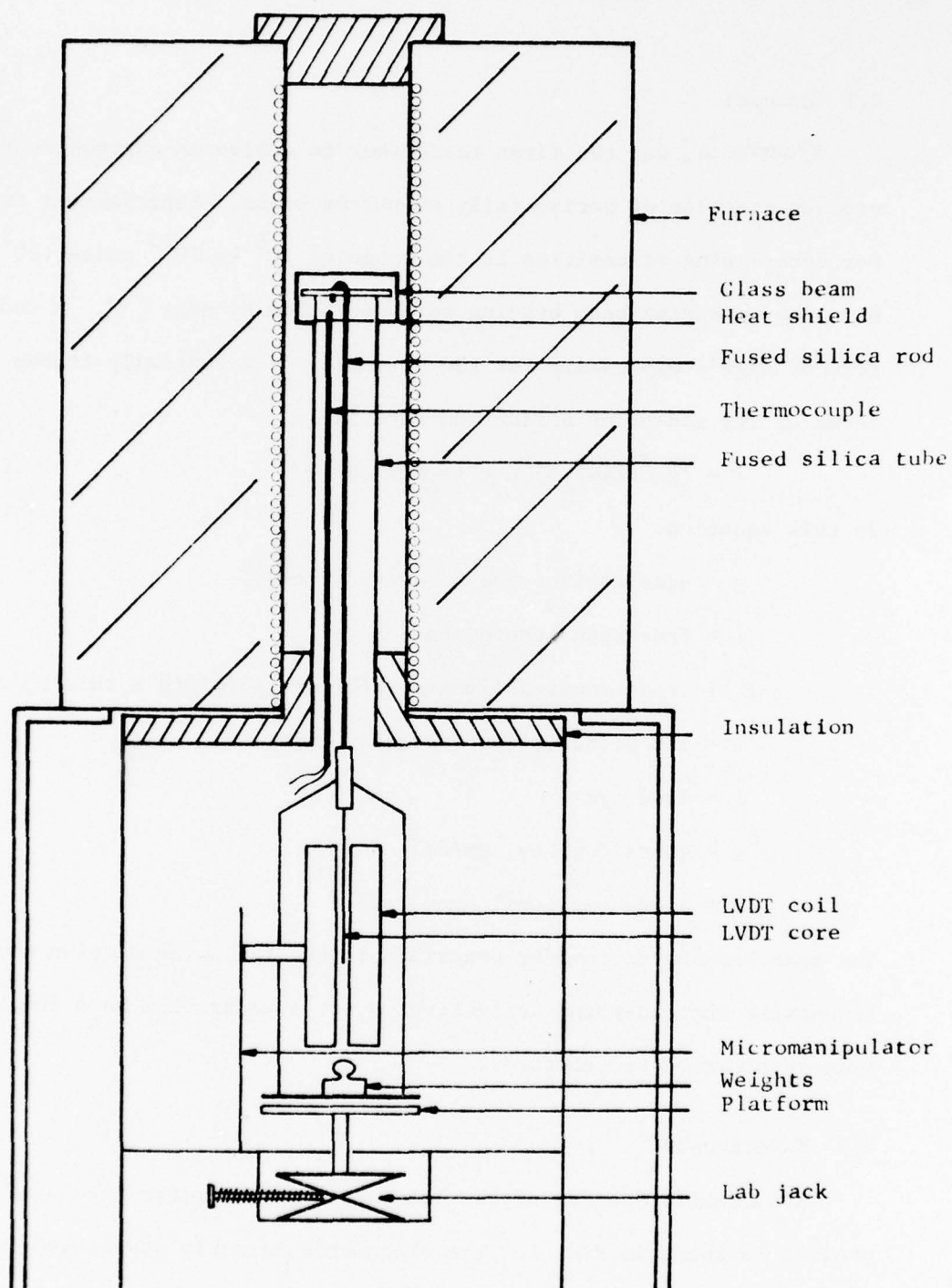


Figure 1. Beam Bending Viscometer.

of the viscometer assembly. The furnace temperature was controlled by an SCR programmable controller. The stainless steel heat shield served to equalize the beam temperature, which was measured utilizing a chromel-alumel thermocouple located approximately 5 mm from the specimen. The glass beam was supported on a fused silica tube cemented to a tripod with leveling screws. Two platinum strips placed on the tube under the ends of the beam prevented the glass beam from sticking to the tube. The inner diameter of the tube is the span length,  $L$ , once the beam begins to sag. A load was applied to the beam by means of a fused silica rod with a hook at one end and a weights pan and the core of an LVDT cemented to the other end. The LVDT coil was mounted on an x-y-z micromanipulator resting on the tripod. The weights pan could be supported or released by means of a lab jack which was also fixed to the tripod.

The glasses with varying amounts of dissolved substrate were prepared according to procedures, and in the apparatus, previously described [2]. The molten glasses at approximately  $800^{\circ}\text{C}$  in platinum crucibles were cast in a stainless steel mold held at approximately  $200^{\circ}\text{C}$ . The 7 cm x 5 cm x 1 cm slabs were annealed, and beams of required thickness was sliced off the slab using a low speed diamond wheel cutter. The beams were polished with  $6\text{ }\mu\text{m}$  diamond grit.

In preparation for an experimental run, the fused silica tube was plumbed by adjusting the leveling screws, the glass beam was placed on the platinum strips, and the loading rod was placed at the center of the beam. The horizontal position of the LVDT coil was adjusted so that the core hung free inside the coil without touching the walls, and the vertical position of the coil was adjusted until the core reached the upper limit

of the operating range of the coil. The furnace was closed around the support tube making sure that there was no physical contact between the furnace and the viscometer assembly. The furnace was heated at a rate of  $3^{\circ}\text{C}/\text{min}$ , and the platform supporting the weight was lowered. The output of the LVDT went to a digital volt meter, and the output of the thermocouple to a digital thermometer. These two instruments, in addition to a digital clock, were imaged with a video camera and recorded on video tape. This procedure was followed because all three variables (deflection, time, and temperature) had to be simultaneously recorded, and the video camera was available and provided a convenient means to accomplish this.

The linearity of the system was investigated by measuring the deflection of a beam at constant temperature; the results of this experiment are shown in Fig. 2. The deflection rate (the slope of the line) is seen to be quite constant, and this rate,  $v$ , when substituted in Eq. 1 along with the beam constants, gives the viscosity. After it was established that the mid-point deflection was a linear function of time at constant temperature, the program controller was used to increase the beam temperature at a rate of approximately  $3^{\circ}\text{C}/\text{min}$ , and the video tape record used to determine the change in deflection over a 20 second time span during which the temperature would change less than  $1^{\circ}\text{C}$ . Typical results for mid-point deflection as a function of time under increasing temperature conditions are shown in Fig. 3.

The stability of the viscometer assembly was checked by replacing the glass beam with a thick fused silica rod, and the system was found to be stable even at  $600^{\circ}\text{C}$ , i.e., no apparent beam deflection was measured. The reliability of the viscometer and the experimental technique was evaluated

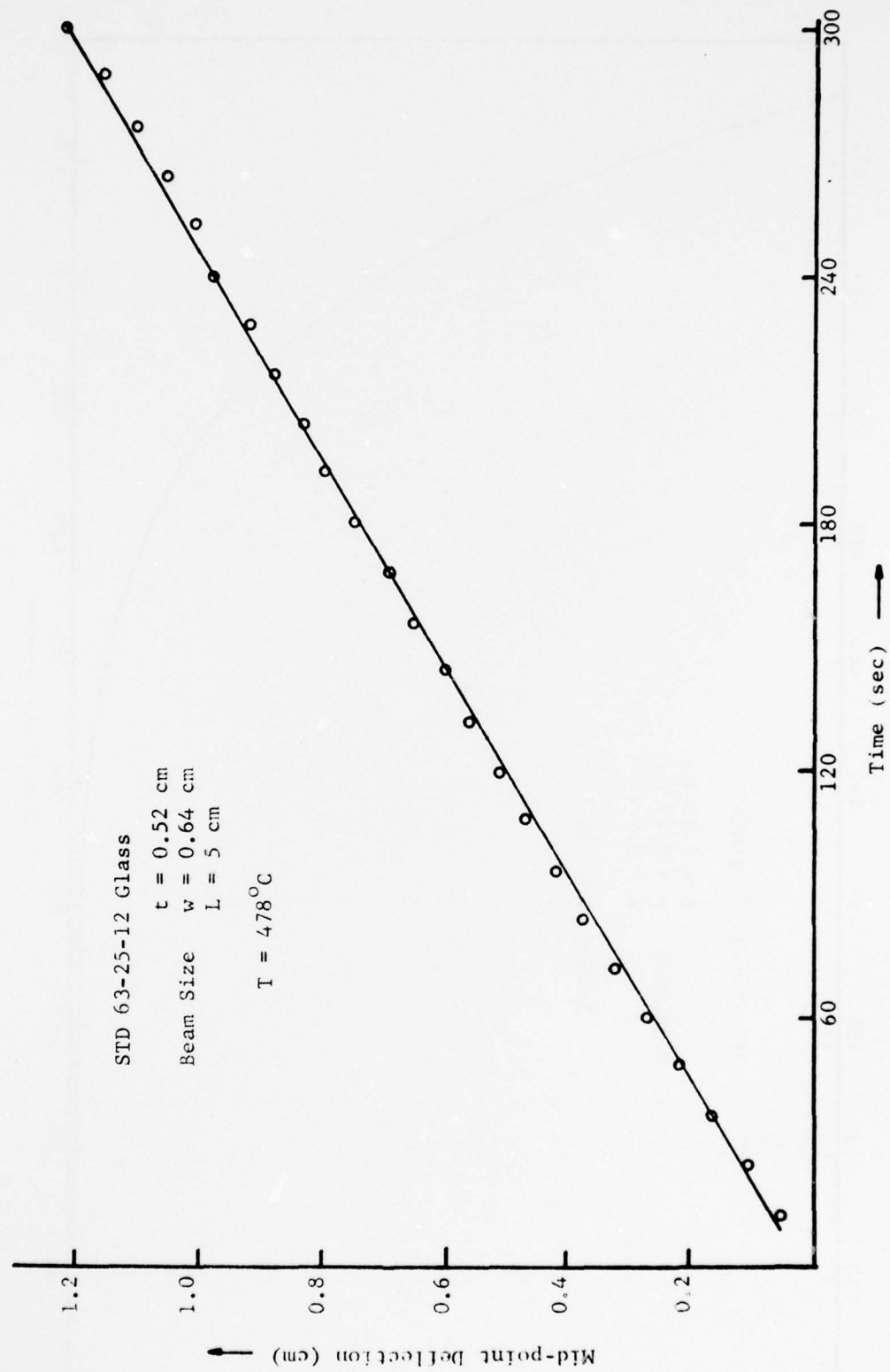


Figure 2. Isothermal Mid-point Deflection of Glass Beam.



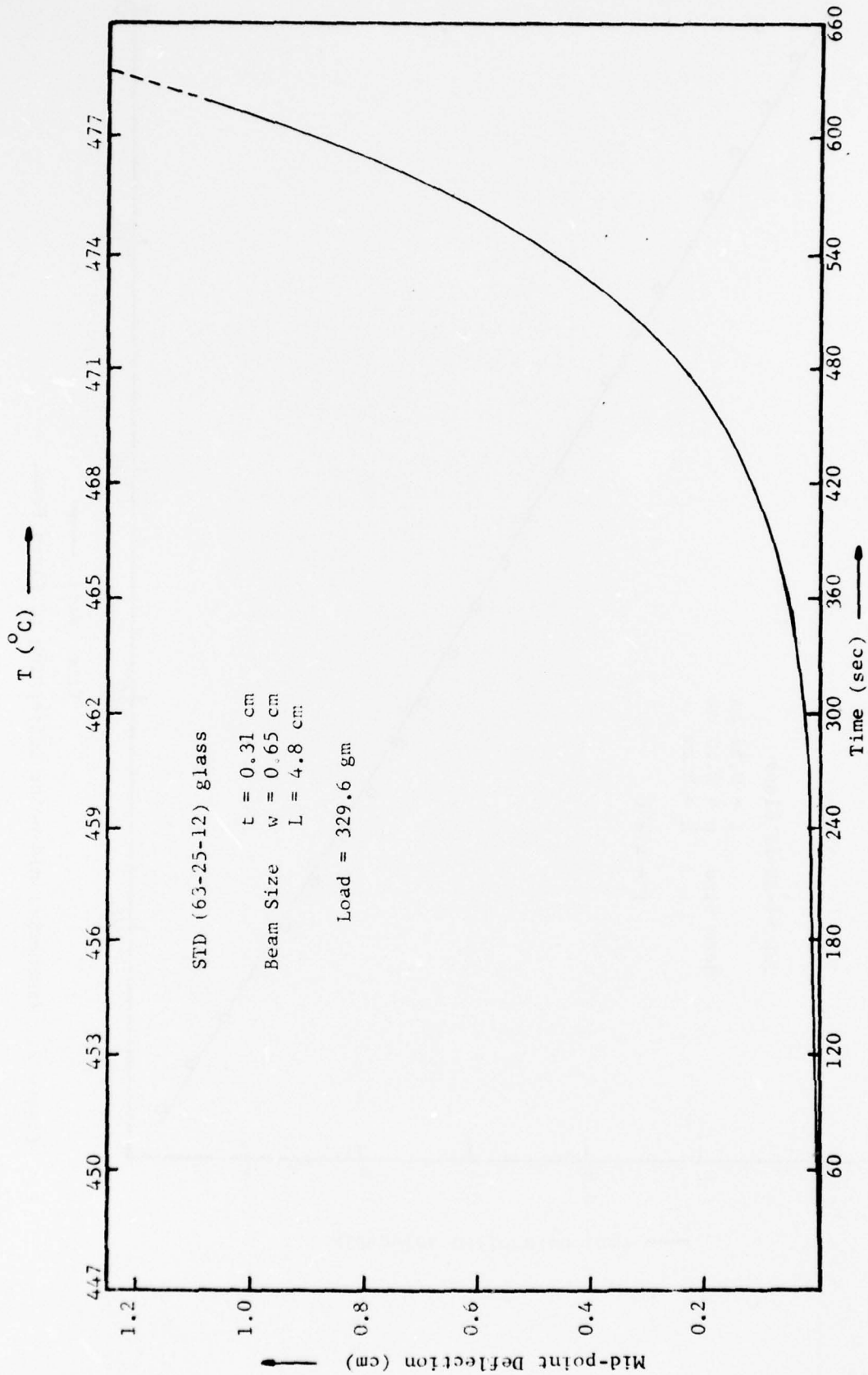


Figure 3. Constant Heating Rate Mid-point Deflection of Glass Beam.

by using Viscosity Standard No. 711 supplied by the National Bureau of Standards. This was a lead silicate glass composition for which the viscosity has been precisely established by several laboratories. Figure 4 shows our results for this glass along with the values predicted by NBS; the agreement is seen to be very good.

### 2.3 Results and Discussion

The viscosities obtained for the standard glass (63w/o PbO-25w/o  $B_2O_3$ -12w/o  $SiO_2$ ) and the standard glass with 2, 4, 6, 8 and 10 weight percent dissolved AlSiMag 614 are shown in Figs. 5-10. These data span the temperature range from near the softening point ( $\eta = 10^{7.6}$  poise =  $10^{6.6}$  Pa·s) to the annealing point ( $\eta = 10^{13}$  poise =  $10^{12}$  Pa·s) for each of the glasses. This is a very important temperature range for several of the important microstructure development processes occurring in thick film resistors [6]. Figure 11 is an Arrhenius plot of the viscosity data for all six glasses. None of the glass compositions give a straight line on Figure 11, which would be the expected behavior if the temperature dependence could be represented by a single activation energy, and the deviation from linearity increases with increasing amount of dissolved substrate in the glass. From Fig. 11, it can be seen that the isothermal viscosity increases by a factor of approximately 20 from the base glass to the base glass with 10 percent dissolved substrate, and an approximate 20 degree spread for equivalent viscosity values among the six glass compositions is observed.

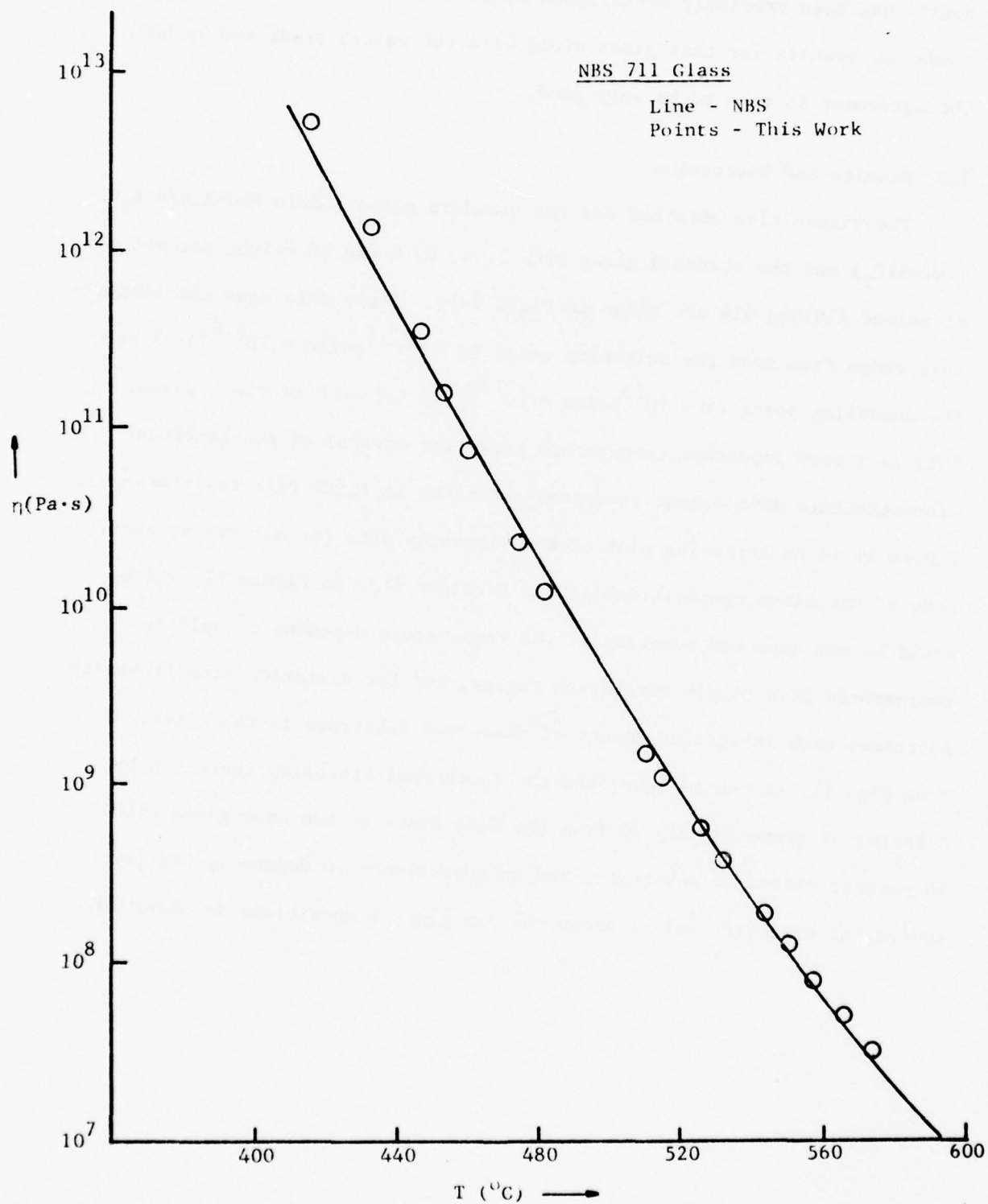


Figure 4. Viscosity of National Bureau of Standards No. 711.

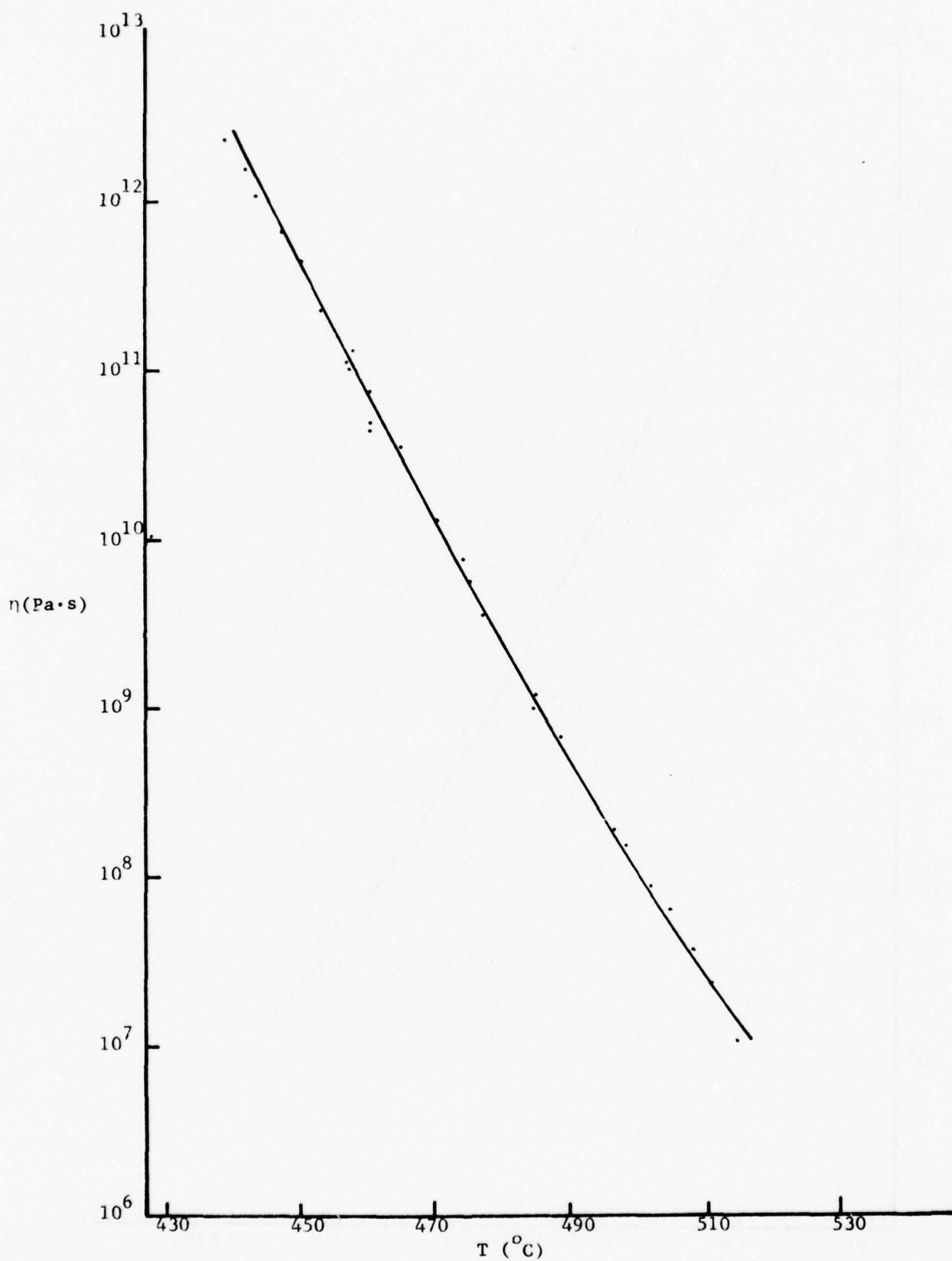


Figure 5. Viscosity of Standard Lead Borosilicate Glass.

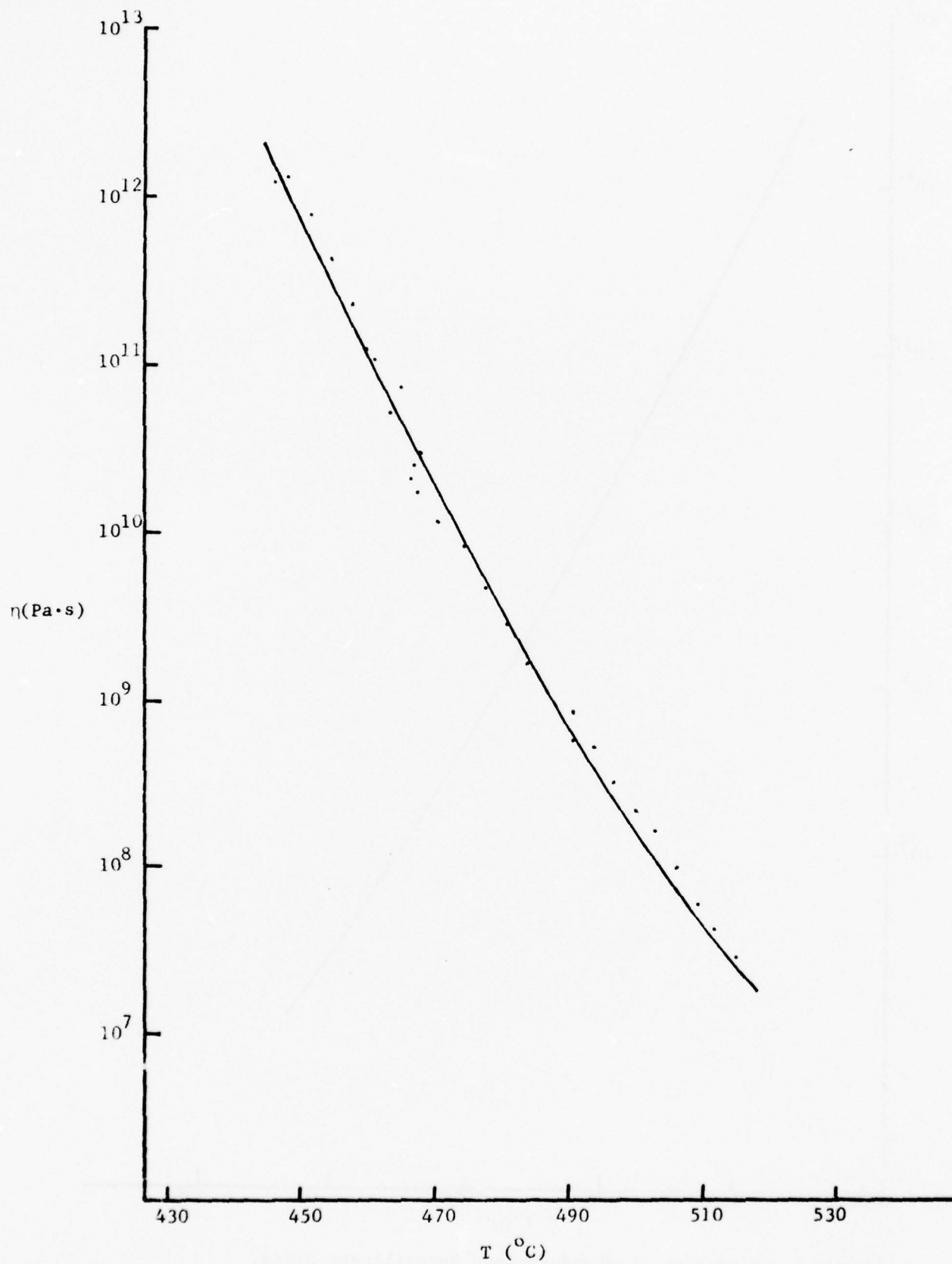


Figure 6 Viscosity of Standard Glass Containing 2 w/o Dissolved Substrate.



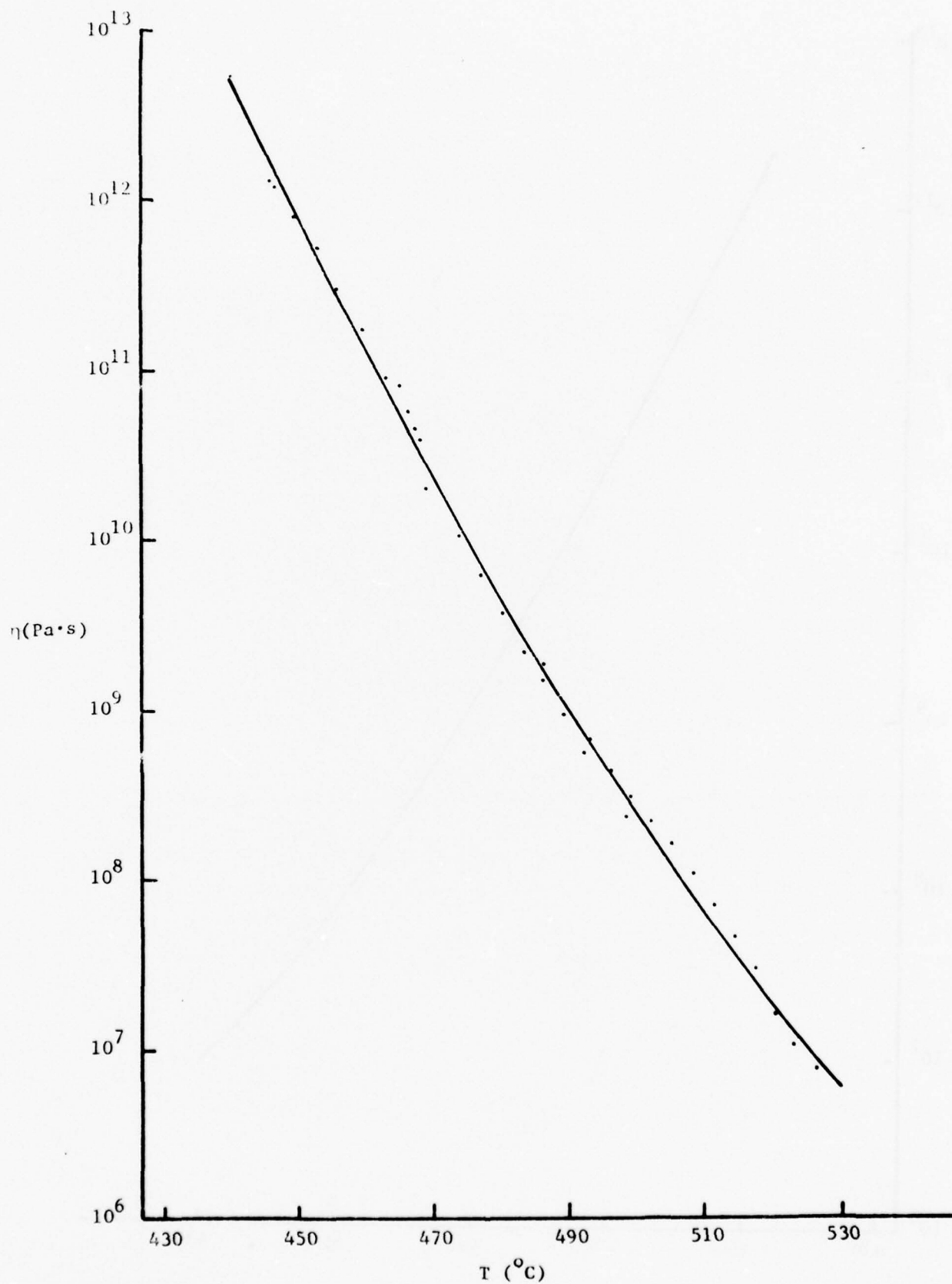


Figure 7. Viscosity of Standard Glass Containing 4 w/o Dissolved Substrate.

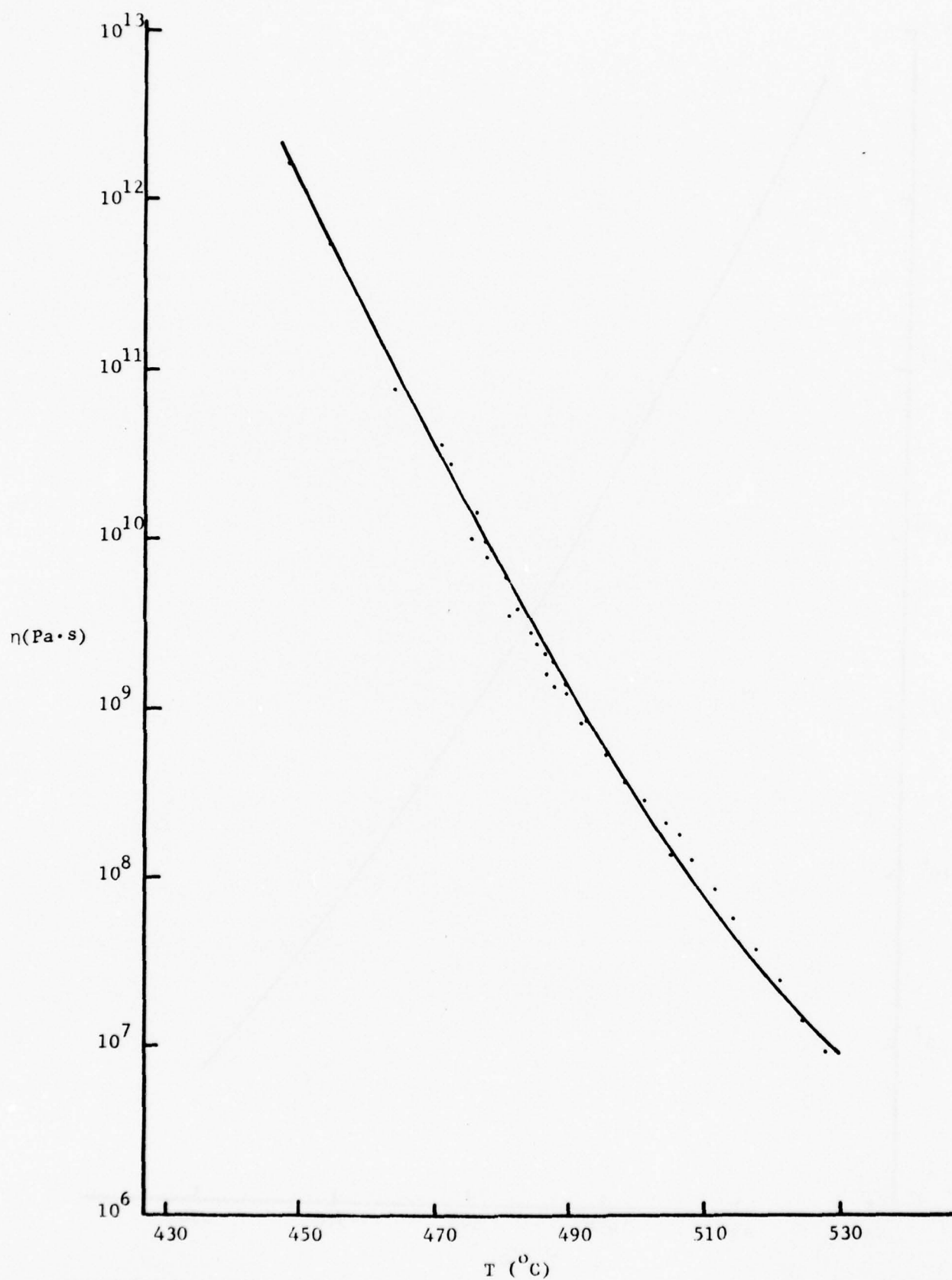


Figure 8. Viscosity of Standard Glass Containing 6 w/o Dissolved Substrate.

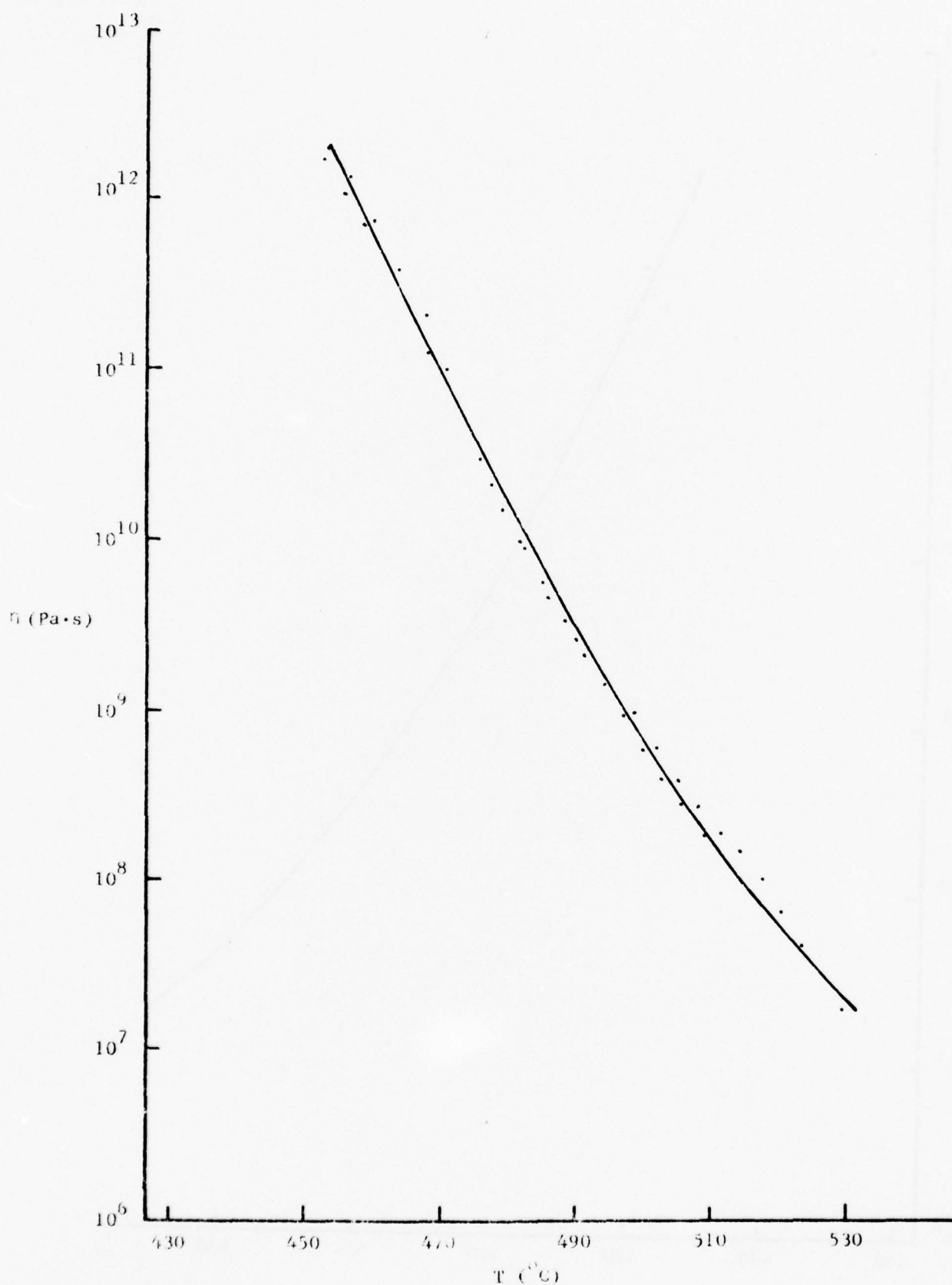
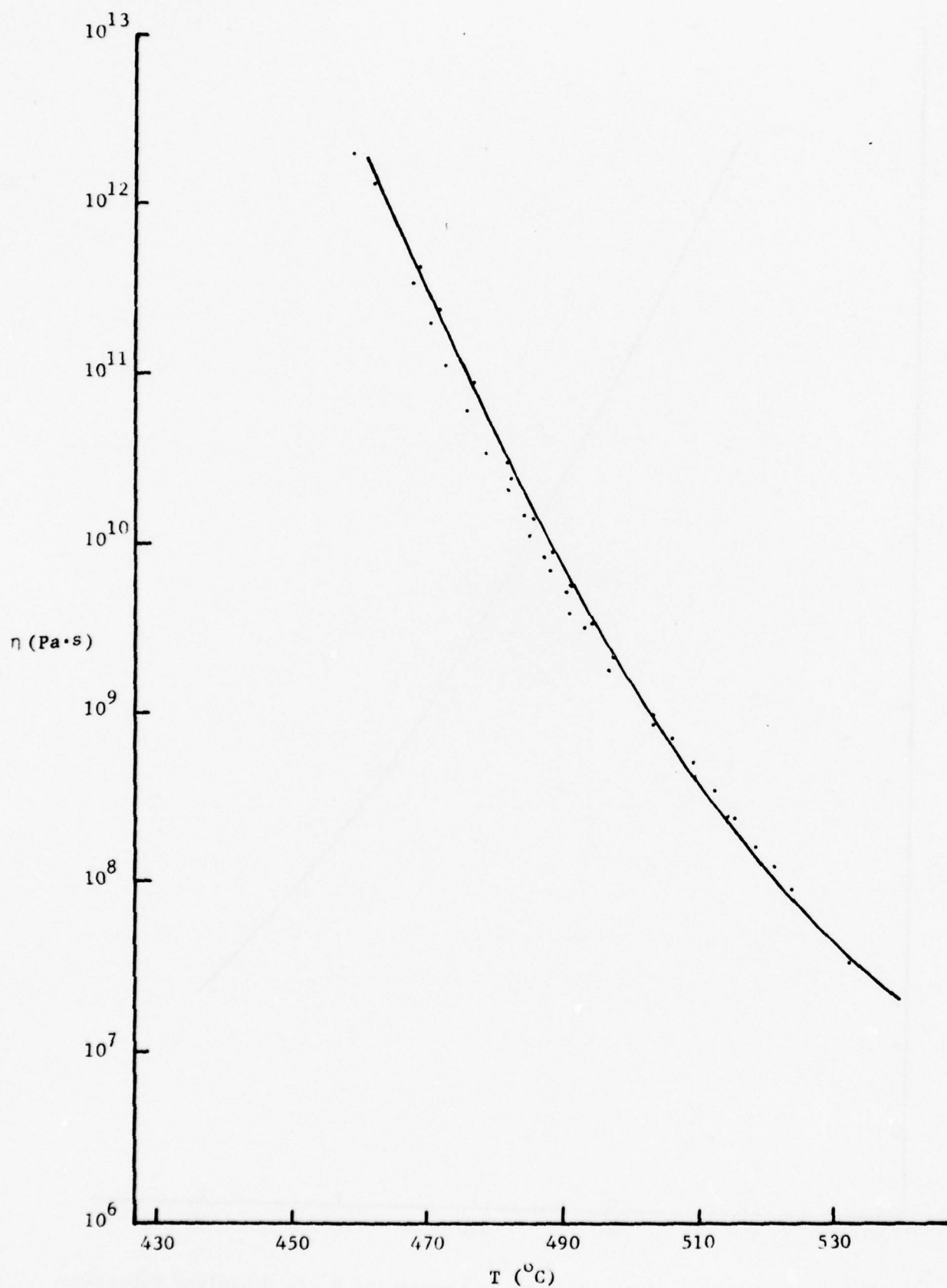


Figure 9. Viscosity of Standard Glass Containing 8 w/o Dissolved Substrate.



... Glass Containing 10 w/o Dissolved Substrate.

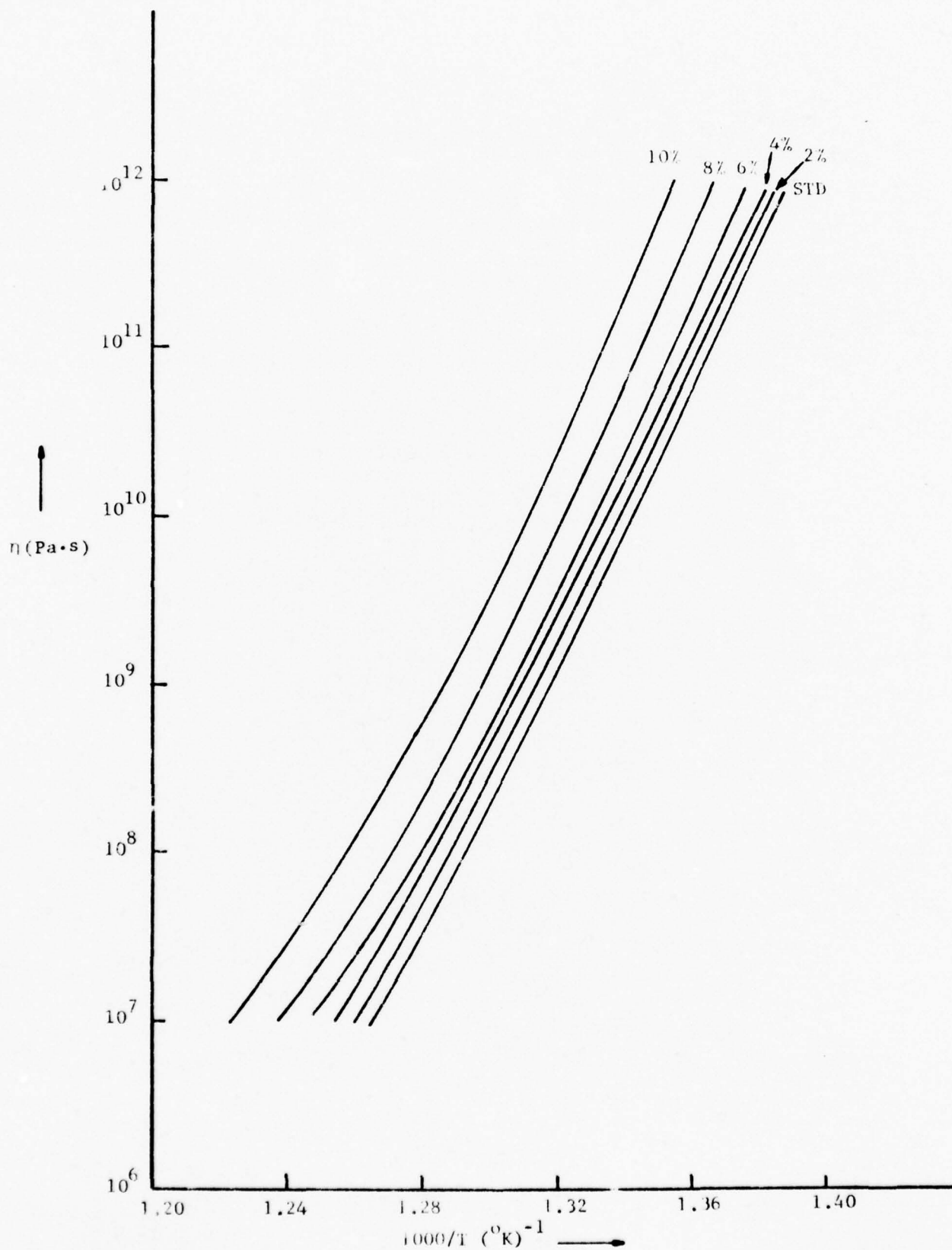
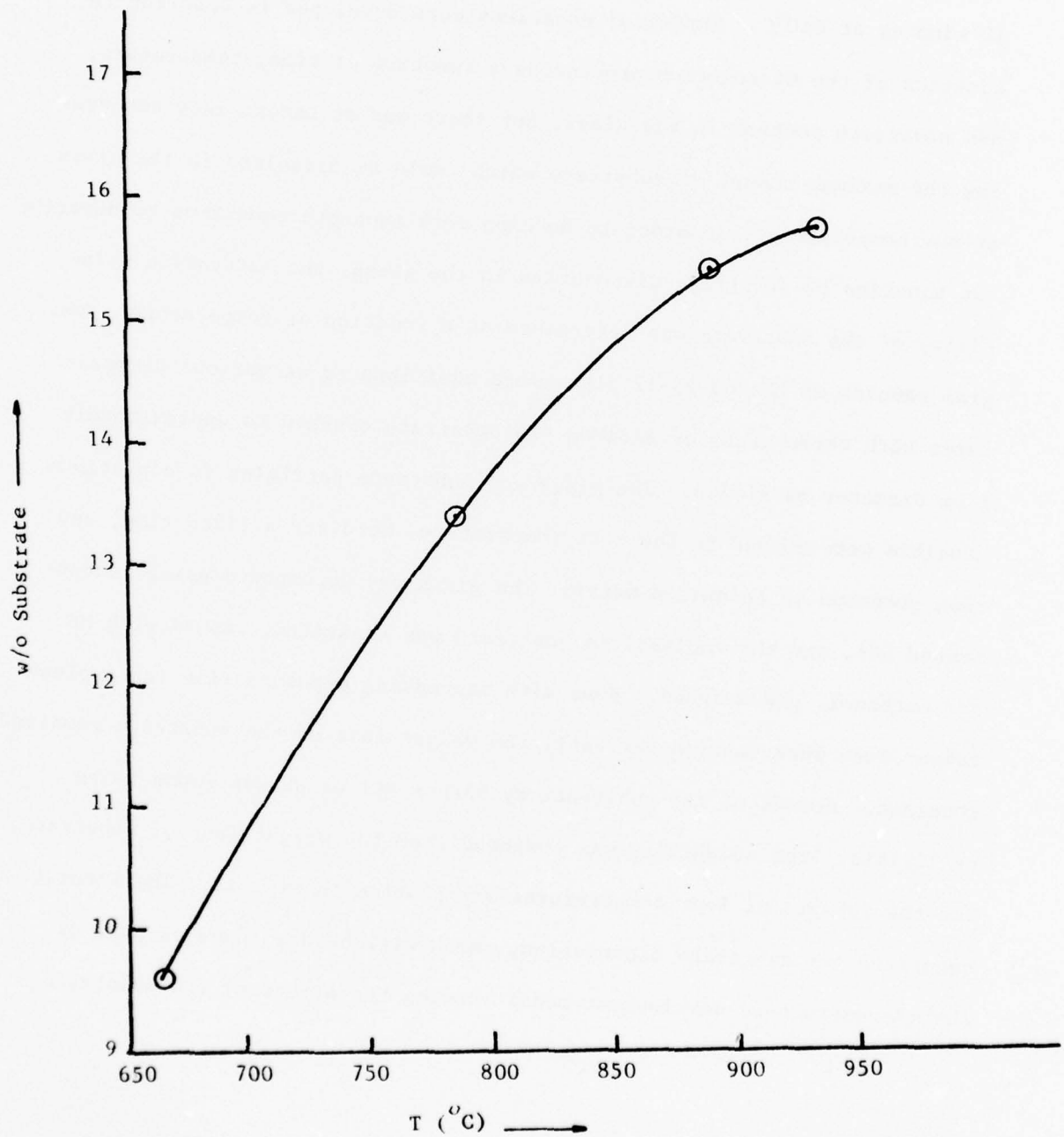


Figure 11 The Effect of Dissolved Substrate on the Viscosity of Standard



### 3. SUBSTRATE SOLUBILITY STUDIES

Previous studies [2] of the kinetics of dissolution of AlSiMag 614 substrates in resistor films containing the 63-25-12 lead borosilicate glass showed a rapid initial dissolution followed by a slower rate during which the substrate content of the glass reached a maximum in approximately 10 minutes at 840°C. Empirical equations were developed to describe the kinetics of the dissolution process as a function of time, temperature, and substrate content in the glass, but there was an uncertainty concerning the maximum amount of substrate which could be dissolved in the glass at any temperature. In order to develop more accurate equations to describe the kinetics of substrate dissolution in the glass, the saturation solubility of the substrate was determined as a function of temperature. Ten gram samples of the 63-25-12 glass were equilibrated at various temperatures with three grams of AlSiMag 614 substrate crushed to approximately 1 mm diameter particles. The glass and substrate particles in a platinum crucible were raised to the test temperature, held for a fixed time, and then quenched in deionized water. The glass was decomposed using concentrated HCl, and the undissolved substrate was separated, washed with HF and methanol, and weighed. Runs with increasing exposure time for a given temperature were carried out until the weight loss of the substrate remained constant. Attack of the substrate by either HCl or HF was found to be negligible. The solubility was computed from the weight loss of substrate, and the results at four temperatures are plotted in Fig. 12. The kinetic equations for substrate dissolution, which will be developed as part of the microstructure development model showing the effect of the substrate,



... of Alsimag 614 Substrate in Lead Borosilicate Glass.

will have to be consistent with the saturation solubility data shown in Fig. 12.

#### 4. RESISTOR STUDIES

##### 4.1 Formulation Blending

The resistor inks used in this project contain 5w/o  $\text{RuO}_2$  relative to glass because this low concentration of conductive phase yields high value resistors with electrical properties that are very sensitive to small changes in microstructure development, and, hence, will magnify the effects of changes in glass composition due to substrate dissolution. Although this composition gives electrical properties which are sensitive to the desired effect, they also are sensitive to other sources of variability. One of these sources is the incomplete blending of either the glass and  $\text{RuO}_2$  powders or the blended powders and the organic screening agent. Another source of variability is the particle size of the glass and the  $\text{RuO}_2$ . The  $\text{RuO}_2$  was from the same lot in all resistors, but different glasses (63-25-12 base glass and 63-25-12 with 4, 6, and 10w/o dissolved AlSiMag 614 substrate) were used in the series of experiments. In order to observe changes in electrical properties arising from differences in glass composition only and not differences in blending or glass particle size, a standard blending procedure was developed and a standardized glass particle size selected.

A sedimentation procedure was developed to yield glass frits of the varying compositions containing only particle of 13  $\mu\text{m}$  or less. A dispersion of 20 to 30 grams of glass to 1000 ml of deionized water was thoroughly mixed and the dispersion down to a depth  $h$  was siphoned off after a time  $t$  as calculated from the integrated Stokes equation.

$$t = \frac{18 \eta h}{g(\rho_g - \rho)d^2}$$

$\eta$  = viscosity of water

$g$  = acceleration due to gravity

$\rho_g$  = glass density

$\rho_l$  = water density

$d$  = particle diameter

The siphoned dispersion was transferred to large dishes for settling, the particle free water siphoned away after an appropriate time, and the glass powders dried. After collecting approximately 30 grams of less than  $13 \mu\text{m}$  particles for each glass, they were blended with 5w/o  $\text{RuO}_2$  by hand for three hours. The blended dry powders were then mixed with 60 v/o of screening agent (10% ethyl cellulose and 90% butyl carbitol) and hand mixed for 30 minutes followed by three hours of continuous blending on the roll mill. During roll mill blending, small amounts of formulation were removed periodically, screen printed on AlSiMag 614 substrates, and fired in a tunnel kiln utilizing a 30 minute firing cycle that included 10 minutes at  $850^\circ\text{C}$ . These experiments provided data on sheet resistance ( $R_s$ ) and its standard deviation ( $\sigma$ ) as a function of the blending time for each ink; the results of these experiments are summarized in Table 1. The blending of each ink was terminated when the standard deviation was less than 5%.



Table 1  
BLENDING RESISTOR INKS

	Standard Glass			4w/o Substrate Glass			6w/o Substrate Glass			10w/o Substrate Glass		
Hours Blended	R <sub>s</sub>	$\sigma$	% $\sigma$	R <sub>s</sub>	$\sigma$	% $\sigma$	R <sub>s</sub>	$\sigma$	% $\sigma$	R <sub>s</sub>	$\sigma$	% $\sigma$
0.0	222K	21K	10%	937K	87K	9%	2.5m	1m	40%	> 300m		
0.5												
1.0	147K	13K	9%	589K	63K	10%				31.7m	23m	73%
1.5							447K	11K	2.5%			
2.0	129K	10K	8%	542K	53K	10%				4.00m	12K	.3%
2.5												
3.0	104K	10K	10%	550K	30K	5.5%						
3.5				436K	20K	4.5%						
4.0	90.7K	2K	2%									

#### 4.2 Conductive Terminations

The current thick film resistor experiments involved resistors produced by screen printing and firing on AlSiMag 614 substrates in order to correlate with data developed on resistors screened and fired on platinum foil which had been reported earlier [2, 3]. The initial approach was to screen and fire the resistors onto substrates with no conductive electrodes, thus limiting the reaction during high temperature processing to resistor-substrate interactions. Contact areas were prepared by sand-abrading the resistor surface, and screenable epoxy electrodes were applied in preparation for electrical testing. However, it was determined that electrodes fabricated in this manner produced resistors that were unstable or ones which would not yield reproducible data.

Experiments were then directed to finding a conductive ink that could be prefired or cofired and be compatible with all resistive inks. Five

commercial inks and one in-house conductive made with platinum powder and the standard 63-25-12 glass frit were evaluated. The resistance of each conductive run and the sheet resistance measured for resistors fired in the belt furnace and batch fired at 930°C for 10 minutes were measured for standard glass resistors with each of the six conductive formulations. In addition to the electrical measurements, the resistor-conductor interface was investigated with a stereo microscope for each sample in order to detect any evidence of nonuniformity in resistor microstructure near the resistor-conductor interface. The results of these experiments are summarized in Table 2.

Table 2  
CONDUCTIVE TERMINATION EXPERIMENTS

Conductor Number	Conductive Particles	Resistance	STD Glass Fired at 930°C, 10 min.	STD Glass Fired in Belt Furnace	Interface Appearance
Du Pont 9308	Pd-Ag	0.50 $\Omega$	182.15K $\Omega$	171.63K $\Omega$	Segregation
Du Pont 9755	Pt-Ag	0.85 $\Omega$	165.57K $\Omega$	188.05K $\Omega$	Segregation
Du Pont 9770	Pt-Ag	0.25 $\Omega$	637.5K $\Omega$	207.77K $\Omega$	Run-out of Res. onto Electrodes
Du Pont 9885	Pt-Au	1.10 $\Omega$	62.9K $\Omega$	110.64K $\Omega$	No segregation, good mixing at interface
Engelhard A-3380	Pt	1.50 $\Omega$	55.11K $\Omega$	101.48K $\Omega$	Segregation
STD Glass 10%	Pt	1.40 $\Omega$	250K $\Omega$	--	Segregation

The most common problem was a segregation (decreased density of  $\text{RuO}_2$  networks in the resistor) near the electrode-resistor interface. Based on these experiments, the Du Pont 9885 platinum-gold conductive was selected for the resistor experiments. It was prefired onto AlSiMag 614 substrates in the desired patterns at  $850^\circ\text{C}$  for 10 minutes after a hold at  $150^\circ\text{C}$  for 15 minutes to remove the organics.

#### 4.3 Resistor Fabrication

The AlSiMag 614 substrates were ultrasonically cleaned in a solution of deionized water and detergent followed by several water rinses and a final acetone rinse. The Du Pont 9885 platinum-gold conductive was screen printed, dried at  $150^\circ\text{C}$  for 15 minutes, and fired at  $850^\circ\text{C}$  for 10 minutes. The substrates were then weighed and numbered prior to screening the resistor inks. After firing the resistors, each substrate was again weighed to determine the weight of the fired resistor in order to calculate the resistor volume and average thickness. Sixty resistors from each of the four formulations were screened, dried at  $130^\circ\text{C}$  for 30 minutes,  $300^\circ\text{C}$  for 30 minutes, and stored in an evacuated desiccator until high temperature firing.

For each firing, four resistors (one standard glass, one 4w/o substrate glass, one 6w/o substrate glass, and one 10w/o substrate glass) were placed on a ceramic tile. They were dried together at  $130^\circ\text{C}$  for 10 minutes to remove any moisture that might have absorbed since screening and then placed in a box furnace at the firing temperature (650, 700, 725, 750, 800, 850, 900, or  $950^\circ\text{C}$ ) for 10 minutes. After cooling to room temperature and weighing, the resistor widths and lengths were measured using a calibrated stage on a stereo microscope. Four resistors of each glass composition (4 tiles) were fired at each temperature.

#### 4.4 Electrical Measurements

The resistance of each sample was measured at room temperature and  $125^{\circ}\text{C}$  to calculate the hot TCR, and then at  $-55^{\circ}\text{C}$  to calculate the cold TCR. In order to make the  $125^{\circ}\text{C}$  and  $-55^{\circ}\text{C}$  resistance measurements quickly and to maintain relatively constant temperatures, hot and cold temperature baths were set up. For the  $125^{\circ}\text{C}$  measurement, an oil bath was heated on a hotplate with a magnetic stirrer. A chromel-alumel thermocouple in the oil bath was utilized for temperature measurement and control. The bath temperature was found to be  $125^{\circ}\text{C} \pm 2^{\circ}\text{C}$  for long periods of time, and samples quickly stabilized (less than 10 seconds) when immersed in the oil. For the  $-55^{\circ}\text{C}$  bath, an immersion cooler (Polyscience VLT 60) was used in a trichloroethylene bath in a dewar flask. The immersion cooler was allowed to reach its base cooling temperature, which would cycle the bath between  $-50$  and  $-60^{\circ}\text{C}$  over approximately a two hour period. Resistors when immersed in this bath stabilized in approximately 20 seconds, and the bath temperature as measured with a chromel-alumel thermocouple immersed in the bath was recorded in addition to the sample resistance.

Each resistor was inserted into a special harness and immersed in a beaker of trichloroethylene at room temperature, and the resistance measured. The sample was then immersed in the oil bath, and the  $125^{\circ}\text{C}$  resistance recorded. The sample was then cleaned in trichloroethylene, cooled to room temperature and the resistance measured again. The room temperature values were always found to be within 0.1 percent of the original value. The sample was then placed in the cold temperature bath, resistance and temperature recorded, and returned to room temperature. This procedure was initially repeated three times for each resistor, but no variation in



resistance at any of the three temperatures was observed. Subsequently, samples were only tested once at 125 and  $-55^{\circ}\text{C}$ .

#### 4.5 Results and Discussion

The results of the room temperature and hot and cold TCR measurements are summarized in Table 3. The lowest firing temperature of  $650^{\circ}\text{C}$  does not appear in Table 3 for any glass composition because all resistors tested greater than  $10^{14}$  ohms. Even at  $700^{\circ}\text{C}$ , the four and six w/o substrate glass resistors could not be measured accurately, and the ten w/o substrate glass resistors were still greater than  $10^{14}$  ohms.

Figure 13 shows the average sheet resistance for each substrate glass resistor as a function of firing temperature. In all cases, the general trend is a very rapid decrease in resistance as firing temperature increases with the resistance higher at each temperature for higher substrate concentration in the resistor glass. These results agree with earlier experiments that suggested a retardation of microstructure development kinetics as the substrate content of the resistor glass increased [6].

Figure 14 shows the hot TCR as a function of firing temperature for resistors made with each of the four glass compositions. The general trend is for an increasing TCR with increasing firing temperature for each resistor glass composition. For firing temperatures of  $850^{\circ}\text{C}$  or below, the hot TCR increased as the amount of substrate in the glass decreased. This trend does not appear to continue above  $850^{\circ}\text{C}$ , which could be indicative of the fact that there is little difference in glass composition at these temperatures due to the dissolution of the substrate during resistor firing. The cold TCR as a function of firing temperature is shown in Figure 15, and the results follow the same general trends as the hot TCR data.



Table 3  
SHEET RESISTANCE, HOT TCR AND COLD TCR FOR SEVERAL  
FIRING TEMPERATURES AND GLASS COMPOSITIONS

Firing Temp	Glass	$R_s$ KΩ/□-mil	$\sigma_{R_s}$	% $\sigma_{R_s}$	Hot TCR ppm/°C	$\sigma_{Hot}$	% $\sigma_{Hot}$	Cold TCR ppm/°C	$\sigma_{Cold}$	% $\sigma_{Cold}$
700°C	STD	30,340	16,680	55%	-233	6.70	2.8%	-403	34.5	8.6%
	4w/o	$10^{12}$								
	6w/o	$10^{12}$								
	10w/o	$10^{14}$								
725°C	STD	1,452	36	2.5%	-195	2.65	1.4%	-325	3.37	1%
	4w/o	17,250	3,550	20.5%	-328	22.3	6.8%	-424	23.0	5.4%
	6w/o	$10^7$								
	10w/o	$10^{14}$								
750°C	STD	282.60	6.59	2.3%	-129	2.81	2%	-260	12.5	4.8%
	4w/o	2,002	315	16%	-196	4.43	2%	-308	10.9	3.5%
	6w/o	12,150	1,580	13%	-245	40.8	16%	-469	51.8	11%
	10w/o	$10^{13}$								

Table 3 (Cont'd)

Firing Temp	Glass	R <sub>S</sub> KΩ/□-mil	σ R <sub>S</sub>	%σ R <sub>S</sub>	Hot TCR ppm/°C	σ Hot	%σ Hot	Cold TCR ppm/°C	σ Cold	%σ Cold
800°C	STD	113.7	4.13	3.6%	-84.9	2.52	3%	-197	3.77	2%
	4w/o	434.2	19.7	4.5%	-110	2.99	3%	-240	3.37	1.4%
	6w/o	676.6	40.3	6%	-204	9.15	4.5%	-344	12.5	3.6%
	10w/o	74,400	36,000	49%	-255	27.6	11%	-439	18.9	4.3%
850°C	STD	80.12	8.93	11%	-41.9	5.09	12%	-137	18.9	14%
	4w/o	211.6	13.9	6.6%	-61.3	2.85	5%	-169	11.0	7%
	6w/o	238.9	11.2	4.7%	-83.9	4.2	5%	-198	21.8	11%
	10w/o	1,418	69.1	4.1%	-122	13.6	11%	-247	16.9	7%
900°C	STD	58.86	4.68	8%	+7.54	2.7	35%	-90.0	4.1	4.6%
	4w/o	87.83	9.51	11%	+18.5	3.3	18%	-70.9	5.4	7.5%
	6w/o	122.2	12.9	11%	+0.36	4.8	1300%	-111	5.9	5.4%
	10w/o	228.7	64.5	28%	+23.6	14.0	59%	-86.6	31.8	37%
950°C	STD	34.63	2.29	6.6%	+94.3	3.5	4%	+11.8	1.9	16%
	4w/o	50.63	7.47	14.8%	+90.4	10.3	11%	+11.6	12.7	109%
	6w/o	79.97	10.8	13.5%	+63.8	4.4	7%	+25.4	3.1	12%
	10w/o	96.83	11.9	12%	+130	4.7	4%	+51.7	4.4	8%

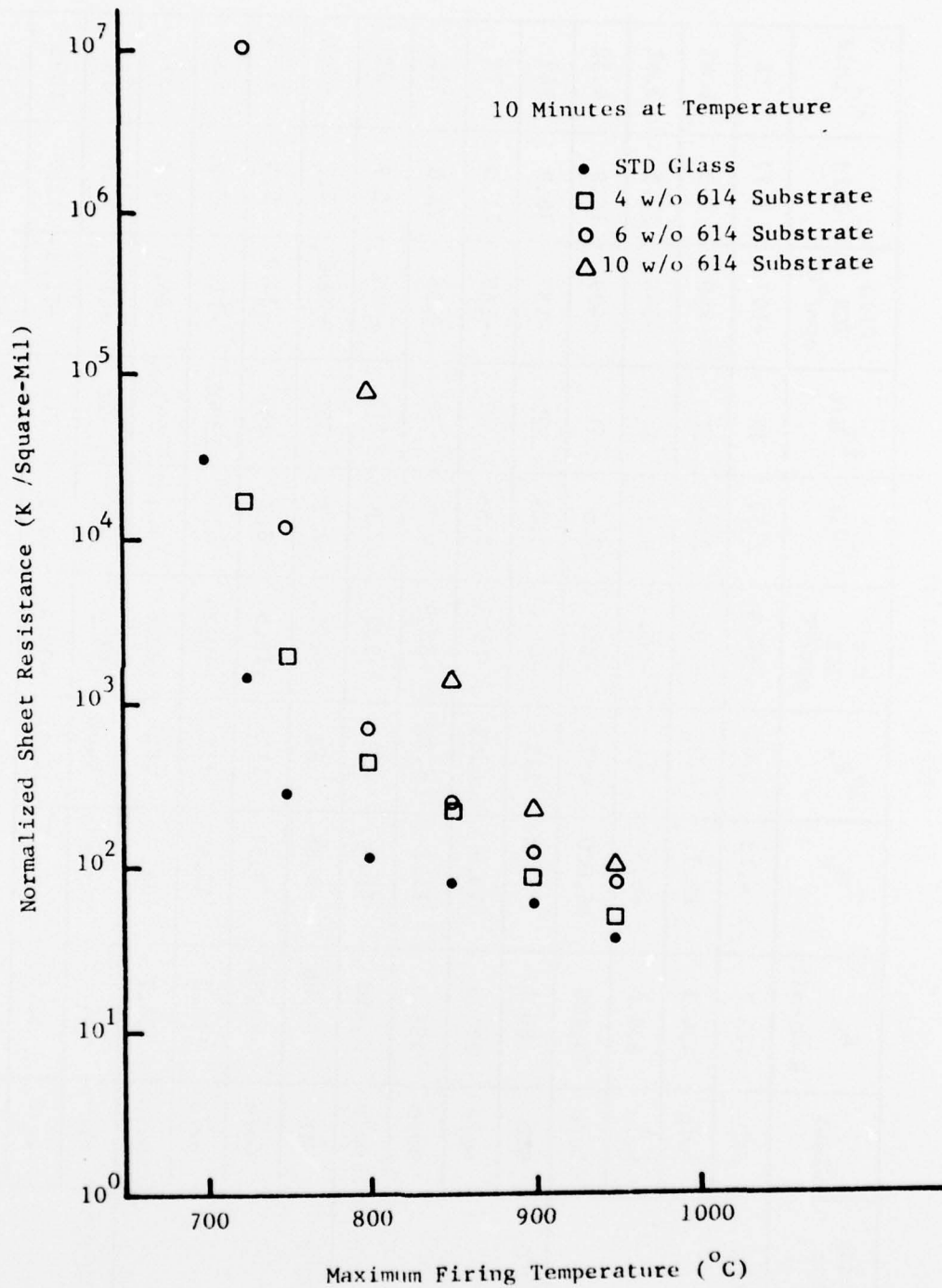


Figure 13. Sheet Resistance as a Function of Firing Temperature.

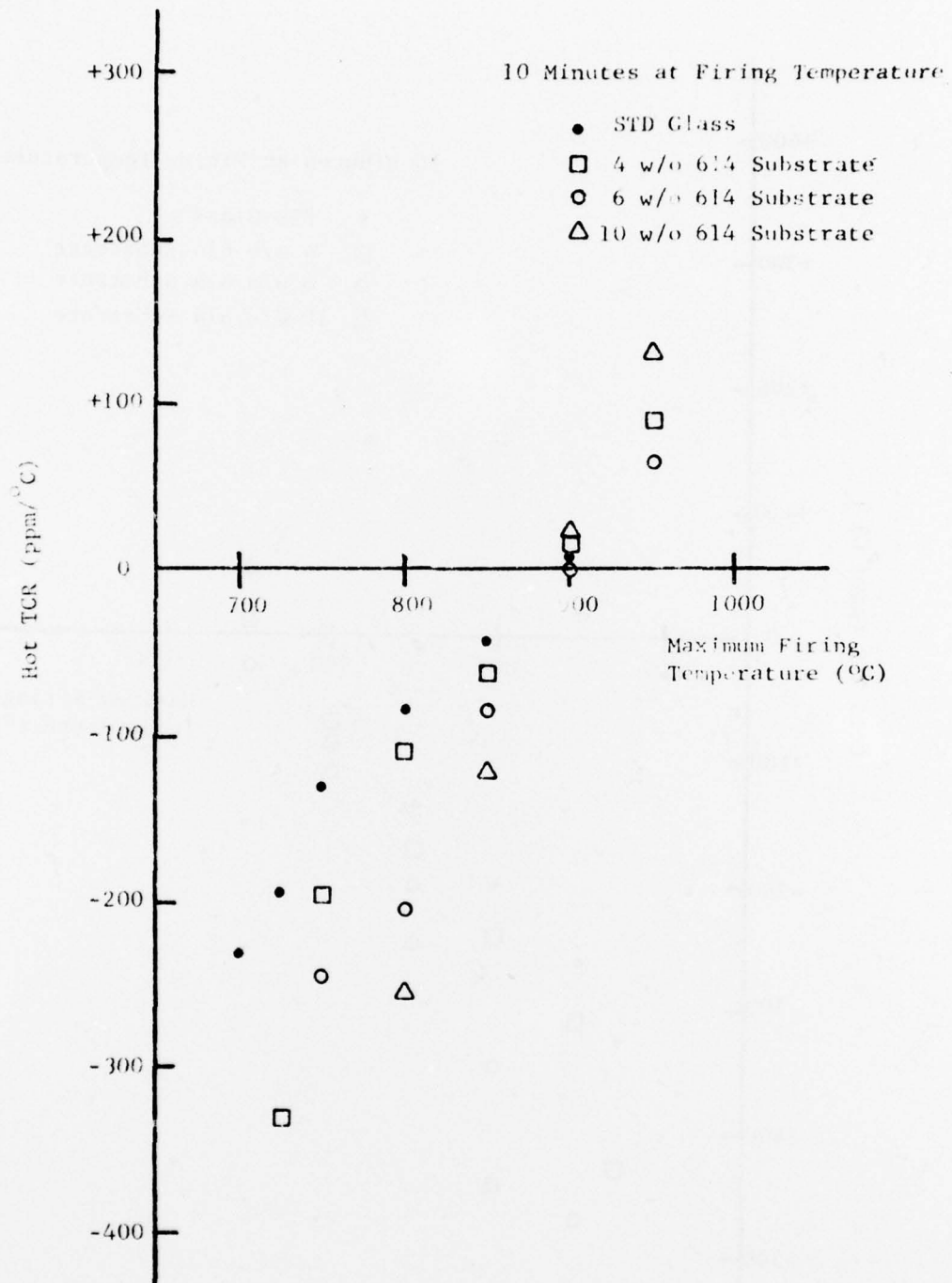


Figure 14. Hot TCR as a Function of Firing Temperature.

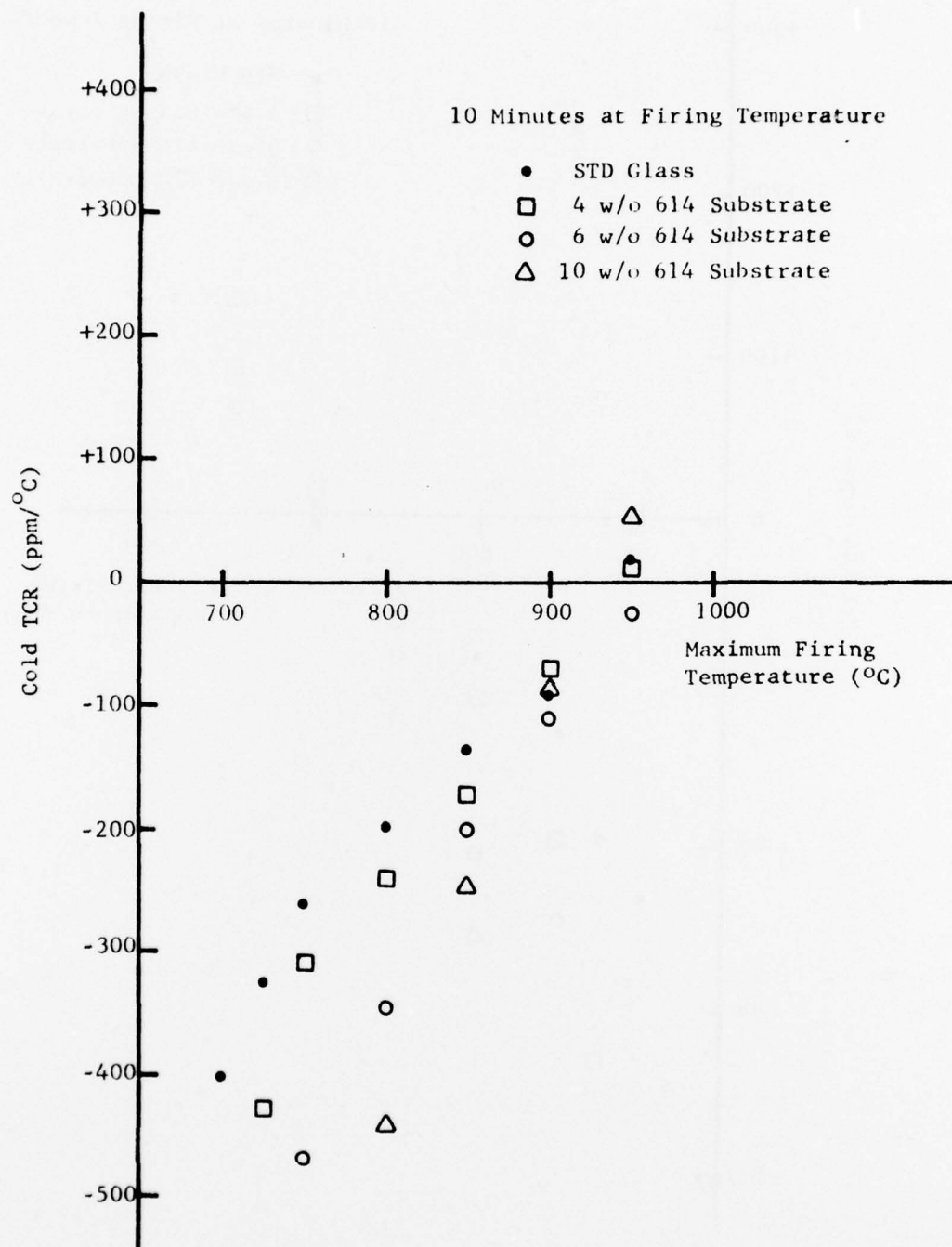


Figure 15. Cold TCR as a Function of Firing Temperature.



A comparison of Figs. 14 and 15 shows that the cold TCR is lower than the hot TCR for each resistor glass at each firing temperature. For example, at 850°C firing temperature the standard glass resistors had a hot TCR of -42 ppm/°C and a cold TCR of -137 ppm/°C.

In addition to demonstrating once again the influence of dissolved substrate on electrical properties of thick film resistors, the data in Table 3 and Figs. 13 - 15 will be utilized in developing a modified charge transport model for thick film resistors which includes the quantitative interactions with the alumina substrates.

## 5. REFERENCES

1. R. W. Vest, "The Effects of Substrate Composition on Thick Film Circuit Reliability," Final Technical Report on Contract No. N00019-76-C-0354, 28 February 1977.
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3. R. W. Vest, "The Effects of Substrate Composition on Thick Film Circuit Reliability," Quarterly Report No. 1 on Contract No. N00019-78-C-0236, 30 May 1978.
4. F. T. Trouton, "Coefficient of Viscous Traction and Its Relation to that of Viscosity," Proc. Roy. Soc. (London), 77, 426 (1906).
5. H. E. Hagy, "Experimental Evaluation of Beam-Bending Method of Determining Glass Viscosities in the Range  $10^8$  to  $10^{15}$  Poises," J. Am. Cer. Soc., 46 (2), 93 (1963).
6. R. W. Vest, "Conduction Mechanisms in Thick Film Microcircuits," Final Technical Report, Purdue Research Foundation Grant Nos. DAHC-15-70-G7 and DAHC-15-73-G8, ARPA Order No. 1641, December 1975.

## 6. FUTURE PLANS

Viscosity and surface tension as a function of glass composition and temperature will be measured at higher temperatures. The kinetics of ripening of  $\text{RuO}_2$  in the glass will be determined as a function of glass composition and the kinetics of the initial stage of liquid phase sintering of  $\text{RuO}_2$  will be calculated from the ripening data and the solubility data. These results will then be correlated utilizing the previously developed models for microstructure development, and the influence of glass composition established. The effects of substrate dissolution on charge transport processes in non-sintered contacts will be determined by fabricating metal-insulator-metal (MIM) structures and measuring the dielectric properties, bulk resistivity and breakdown characteristics of the glass as well as the current-voltage characteristics of the MIM all as a function of glass composition. The dependence of both the glass properties and the electrical properties of the non-sintered contacts on glass composition will be incorporated into a revised charge transport model for thick film resistors.

7. STATEMENT OF ESTIMATED COSTS

Contract No. N00019-78-C-0236

February 1, 1978 - January 31, 1979

Beginning Fund Balance	\$ 65,000
Funds Expended Through 7/31/78	<u>19,620</u>
Funds Remaining	\$ 45,380

Planned Expenditures (Approximate)

August	\$ 9300
September	9300
October	6695
November	6695
December	6695
January	6695